CHLORIDE TOXICITY IN THE UPPER SOUTH FORK OF THE NEW RIVER: IMPLICATIONS FOR WATERSHED HEALTH AND AQUATIC LIFE

A Thesis
by
JAMES ZEBULON SANDERS

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APPROVED BY:

Derek J. Martin, Ph.D.
Chairperson, Thesis Committee

Jeffrey Colby, Ph.D.
Member, Thesis Committee

Chuanhui Gu, Ph.D.
Member, Thesis Committee

Kathleen Schroeder, Ph.D.
Chairperson, Department of Geography and Planning

Max C. Poole, Ph.D.
Dean, Cratis D. Williams School of Graduate Studies

Abstract

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IMPLICATIONS FOR WATERSHED HEALTH AND AQUATIC LIFE

James Zebulon Sanders
B.A., Appalachian State University
M.A., Appalachian State University

Chairperson: Derek J. Martin, Ph.D.

This Study investigates Chloride (Cl^-) trends in the Upper South Fork of the New River associated with the transport of de-icing road salts into stream networks through the mechanism of surface water runoff. Collection of water samples over the course of one year (August 2016- August 2017) provided Cl^- concentration data both in association with major precipitation events and during base flow conditions for six sub-basins of the Upper South Fork of the New River Watershed. Correlation analysis examined the relationship between both annual and seasonal Cl^- concentrations and land-use/ land cover characteristics for each sub-basin. The relationship between specific conductivity and Cl^- enabled the extrapolation of Cl^- from a six-year conductivity record provided by in-situ data loggers at each sub-basin outlet. The results show a strong correlation between impervious surfaces and Cl^- concentrations. Results also show a strong seasonal signature in moderately to highly developed sub-basins where Cl^- levels peak during the winter months in conjunction with road salt application. Further, this research demonstrates the hysteretic response of Cl^- to

stream discharge in the Upper South Fork of the New River Watershed, highlighting the inadequacy of simple Ordinary Least Squares regression as a means for modeling the relationship between Cl^- and discharge. Finally, the six-year Cl^- record, which shows concentrations in excess of toxicity thresholds with much higher frequency in the sub-basins with comparably higher impervious surface, highlights the importance of this research for on-going and future management-related discourse in the Upper South Fork of the New River.

Acknowledgments

Firstly and foremost, I am profoundly appreciative to my thesis committee chair and advisor Dr. Derek Martin, whose limitless patience and knowledge has provided indispensable guidance during this process. Dr. Martin's enthusiasm and expertise has made the challenges of research infinitely more surmountable and captivating for me. I could not feel more fortunate in the mentorship I have received. Thank you so much.

I am also deeply appreciative to my thesis committee members Dr. Colby and Dr. Gu. Their constructive feedback has provided insight and encouragement that has greatly improved the caliber of my research.

Lastly, I want to acknowledge my family, friends, and the many wonderful individuals in the geography department. My accomplishments might not have been possible, and certainly would have been less enjoyable without the support and camaraderie of my new friends in the geography masters' program, the friends who have been instrumental in my life for far longer, and the family that has been encouraging and loving throughout my entire life. I owe all of you so much.

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Introduction

The Upper South Fork of the New River Watershed (USF-NRW), located in the Appalachian Mountains of Western North Carolina, is home to extraordinary biological diversity and pristine water resources in the form of mountain headwater streams. These characteristics are a result of the region's topography, climate, elevation, latitude, and land use/ land cover and are of fundamental importance to both the culture and economy of the region. As the impacts of anthropogenic activity and land-use change continue to increase in the USF-NRW, research and conservation efforts concerning stream health will become critical for future efforts to preserve the ecological integrity of this valuable watershed.

A growing water quality concern in the USF-NRW is chloride (Cl^-) toxicity resulting from the application of deicing salts (NaCl) throughout the watershed. Deicing salt is applied to roads during winter months, and is critical to public safety. However, the resulting addition of Cl^- to the environment has profound effects on soil chemistry, groundwater, stream water chemistry, and aquatic life (Cañedo-Argüelles et al. 2013, Cockerill, Anderson, Harris & Straka, 2017). Although considerable research has been conducted on the effects of Cl^- in different regions, with an emphasis on mid and high latitude environments (Betts, Gharabaghi & McBean, 2014, Corsi, De Cicco, Lutz & Hirsch, 2015), relatively little attention has been given to Cl^- levels in the Southeast, where the necessity of deicing is comparatively infrequent. In this regard, the southern Appalachian Mountains are a geographical exception that receive numerous frozen precipitation events throughout the winter as a result of higher elevation. Additionally, many of the winter weather events in the USF-NRW are followed by high intensity melting events, or even rainfall, which can produce considerable surface runoff. This runoff, exacerbated by the steep local relief inherent in the topography of the southern Appalachians, contributes to hydrologic flashiness of streams in the region and thus has the potential to produce acute pollutant toxicities for streams within the USF-NRW.

This research investigates annual Cl^- trends in streams of the Upper South Fork of the New River Watershed, North Carolina. A better understanding of annual Cl^- trends in the USF-NRW will provide a baseline for monitoring water quality, and will contribute to the on-going discourse related to the use of deicing salts, information that will be important in ongoing and future conservation efforts that pertain to the USF-NRW and similar watersheds in Southern Appalachia.

Literature Review

Cl^- in the Environment

Chloride ions, which occur naturally in our environment, exist in all igneous and sedimentary rocks, in the living tissue of all plants and animals, and in earth's oceans with an average concentration of 19,000 mg/L. The presence of naturally occurring Cl^- extends throughout the entire hydrosphere and arrives in our river systems primarily through atmospheric deposition and geologic weathering (Feth, 1981).

In addition to natural sources of Cl^-, anthropogenic activity substantially contributes to Cl^- in the environment. Human waste, in septic tanks or wastewater treatment plants, can contribute to Cl^- levels (Novotny, Sander, Mohsensi & Stefan, 2009), as can the use of potassium based fertilizers in agriculture (Böhlke, 2002). Paramount to other anthropogenic sources of Cl^-, the greatest contribution to Cl^- levels in our streams and rivers results from the use of de-icing agents, the most predominant of these being sodium chloride (NaCl), or rock salt (Kelly et al. 2008).

Application of De-Icing Salt in North America

Sodium chloride (NaCl), when dissolved, can lower the freezing point of water to 18 degrees Fahrenheit, making it a valuable tool for deicing roads and sidewalks. The application of de-icing salt in North America was first adopted during the 1950s and has since rapidly increased in popularity. By 2008 the United States was applying 15 million metric tons of NaCl to our road and sidewalk networks, yet this number had grown to nearly 24 million metric tons by 2014 (The Salt Institute, 2017). In the Boone Creek sub-basin alone, Town of Boone and Appalachian State University crews apply between 200 and 2000 tons of NaCl annually.

Application of this enormous quantity of salt is not without justification. Data from the United States Department of Transportation (USDOT) shows that accidents on snowy or icy roads account for an average of more than 1800 deaths and nearly 140,000 injuries annually (USDOT, 2017). Research from the American Highway Users Alliance has shown that the proper application of road salt and effective snow removal can reduce the number of traffic incidents associated with wintry conditions by 88 percent (Kuemmel & Hanbali, 1993).

Environmental Impacts of Chloride

Road salt application has led to elevated levels of Cl^- in soils, groundwater, lakes and rivers. Chloride ions are easily transported and consequently arrive in rivers and streams through leaching from groundwater and from stormwater runoff or other forms of overland flow.

Recent research has shown a rapid increase in Cl^- concentrations in freshwater bodies in several regions of the United States (Corsi, Graczyk, Booth, Richards & Geis, 2010, Dailey, Welch & Lyons, 2014, Kelly et al. 2008). The United States Environmental Protection Agency (USEPA) considers a Cl^- concentration of 860 mg/L averaged hourly as the threshold for acute toxicity, and levels as low as 230 mg/L for a four-day moving window as chronically toxic for some aquatic biota, as well as being toxic for human consumption (USEPA, 1988, 1998). In recent research, the USGS found that 55 percent of northern streams in a study had levels exceeding chronic toxicity levels and 25 percent of the streams had Cl^- levels in excess of the acute toxicity threshold (Corsi et al. 2010, Corsi et al. 2015).

Although the impact of Cl^- varies considerably by species and stage in life, concentrations of Cl^- at or above the chronic and acute toxicity levels have shown profoundly negative effects on aquatic ecosystems (Corsi et al. 2010). These impacts include reduced abundance of zooplankton (Sarma, Nandini, Jesús, Israel & Leticia, 2006) reduced growth of salmonid fish (Hintz & Relyea, 2017) and reduced survival rates for macroinvertebrates (Blasius & Merritt, 2002) such as crustaceans and amphibians (Karraker, Gibbs, & Vonesh, 2008). High Cl^- concentrations have been implicated in altering patterns of succession in aquatic vegetation (Wilcox, 1986), impairing the health of roadside trees (Czerniawska-Kusza, Kusza & Duzyński, 2004) and even facilitating the dominance of salt tolerant invasive species over native vegetation (Richburg, Patterson & Lowenstein, 2001). Additionally, a Cl^- level at or exceeding 250 mg/L, is considered unpotable for human consumption (USEPA 1988, 1998).

Cl^- in Southern Appalachia

Similar to regions in the Midwest and Northeast United States, Southern Appalachian Mountain communities apply deicing salts to roads during the winter months. The climate of the USF-NRW, which frequently produces frozen precipitation, necessitates the use of de-icing salts or brine for public safety. Despite this similarity to Northern U.S. climate types, many winter weather events in the USF-NRW are followed by high intensity melting, or rainfall. This suggests that the hydrologic controls responsible for Cl^- transport in the USF-NRW are influenced by surface runoff as well as groundwater leaching.

Previous research for the Boone Creek catchment of the USF-NRW used conductivity as a proxy for Cl^- which revealed that Boone Creek experienced chronic toxicity levels of Cl^- approximately 10% of the year and acute toxicity levels approximately 2% of the year (Cockerill et al. 2017). Considering the profound impacts Cl^- can have on water quality and aquatic life, it has become increasingly important to improve our understanding of hydrologic controls and Cl^- toxicity in the USF-NRW.

Research Design

Objectives

The objectives of this research were 1) Investigate the relationship between Cl^- and sub-basin road network and impervious surface characteristics in the USF-NRW, 2) Investigate seasonal variations in Cl^- and make comparisons between USF-NRW sub-basins, 3) Investigate the relationship between Cl^- concentrations and stream discharge in the USF-NRW, and 4) assess six years of Cl^- toxicity within the sub-basins of the USF-NRW using specific conductivity.

Study Area

This research took place in the Upper South Fork of the New River Watershed (USF-NRW). The USF-NRW is a headwater watershed of the New River, approximately 80 km^2 in size, located in Watauga County, North Carolina (Figure 3.1). Land-use and land cover (LU/LC) throughout this sub-basin is representative of the LU/LC for many of the watersheds in the Blue Ridge Mountains. Land cover consists predominantly of forested hillsides with agricultural land and urban development limited to floodplains, valleys, and areas where the local relief is less extreme. Elevations within the study area range from approximately 4680 feet above sea level on the eastern ridge of Rich mountain, to approximately 3120 feet above sea level at the basin outlet. The mountainous nature of the area restricts where development can occur, and the density of development, and impervious surfaces are primarily concentrated in the towns of Boone and Blowing Rock.

The Town of Boone, and the USF-NRW are located in a Dfb Köppen climate region, which is the mild, cool summer subtype (a rarity for locations in the Southeastern U.S.) of the greater humid continental climate region. Daily mean temperatures in Boone range from 20.3 °C (68.54 °F) in July to -0.4 °C (32.72 °F) in January. Average annual precipitation in Boone is 52.7 inches, with monthly averages ranging from 3.59 inches in October to 5.10 inches in June, and average annual snowfall is 34.6 inches, with monthly averages ranging from 0.1 inches in October to 10.3 inches in January. Very little streamflow data is available for the USF-NRW as the United States Geological Survey only maintains one real-time stream gage in the Upper New River Basin (Gage #03161000), and it is located on the South Fork of the New River, near Jefferson, NC, much farther downstream of the study area.

Field data for this research was collected from six water quality/stage monitoring stations located throughout the USF-NRW. Five stations are located on tributaries of the Upper South Fork of the New River, and one station is on the Upper South Fork of the New River, and thus serves as the outlet for the entire study region (Figure 3.1, Table 3.1). Monitoring stations were established, and are maintained by the Appalachian Aquatic Science Research Team (AppAqua) at Appalachian State University, and have been in operation since 2010. Each monitoring station consists of an in-situ water quality sonde that measures pH, temperature, conductivity, and depth (stage) at 15 minute intervals, and a staff gage (Figure 3.2). These sites/streams were originally chosen for monitoring as they serve as the outlets of basins representing the spectrum of land-uses, from relatively little human influence (Goshen Creek) to a high level of human activity and urbanization (Boone Creek). The North Carolina Department of Environmental Quality (NCDEQ) water classifications for the selected streams are listed in Table 3.1. It should be noted in this study that the ‘State Farm’ sub-basin denotes the location of the monitoring site, but the State Farm watershed is synonymous with the entire USF-NRW watershed, which encompasses all five of the other tributaries.

Table 3.1. Stream classifications (NCDEQ) and collection site locations (NCDEQ)

Stream name	**NCDEQ Classification and Description**	**Drainage Basin Area (km^2)**
Boone Creek	Aquatic Life, Secondary Recreation, Fresh Water; Trout Waters; Protected Headwaters	5.29
Hodges Creek	Aquatic Life, Secondary Recreation, Fresh Water; Trout Waters; Protected Headwaters	3.11
Winkler's Creek	Water Supply II – Undeveloped; Trout Waters; High Quality Waters	6.99
Middle Fork South Fork New River	Water Supply IV- Highly Developed; Protected Headwaters	30.6
Goshen Creek	Water Supply IV- Highly Developed; Trout Waters; Protected Headwaters	6.01
South Fork New River (State Farm)	Aquatic Life, Secondary Recreation, Fresh Water; Protected Headwaters	79.55

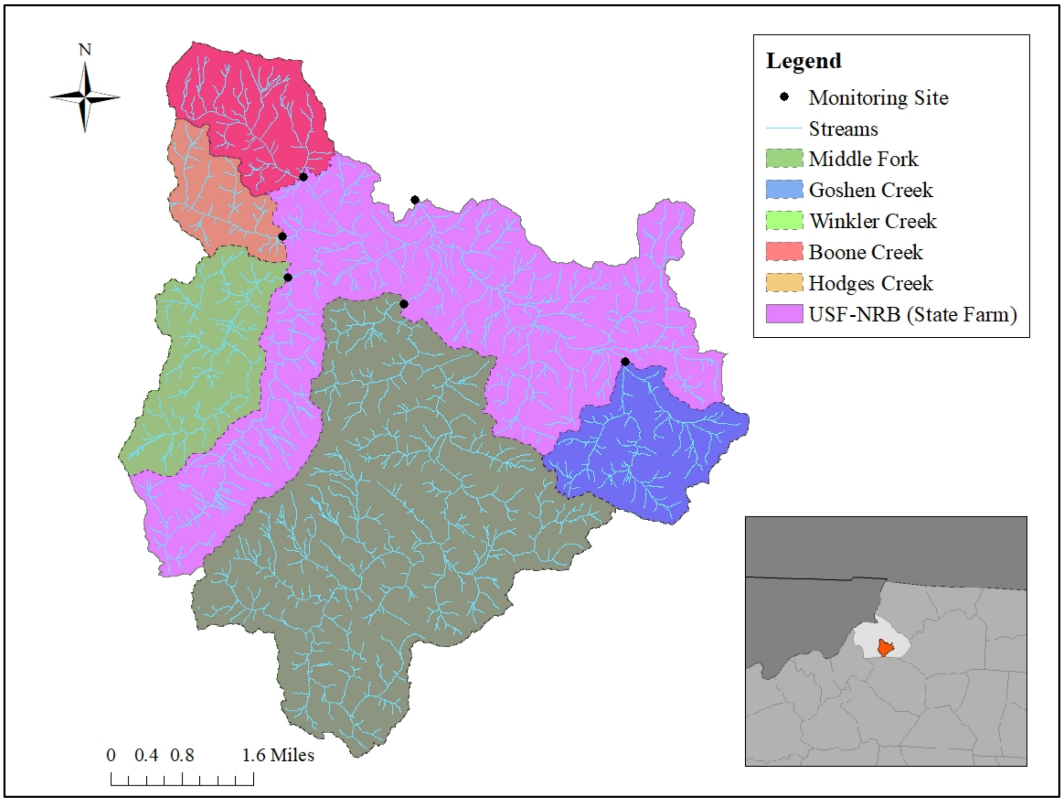

Figure 3.1. Monitoring stations and contributing drainage areas located in the Upper South Fork of the New River basin. . Note: The drainage area for the State Farm monitoring station includes all others as sub-basins.

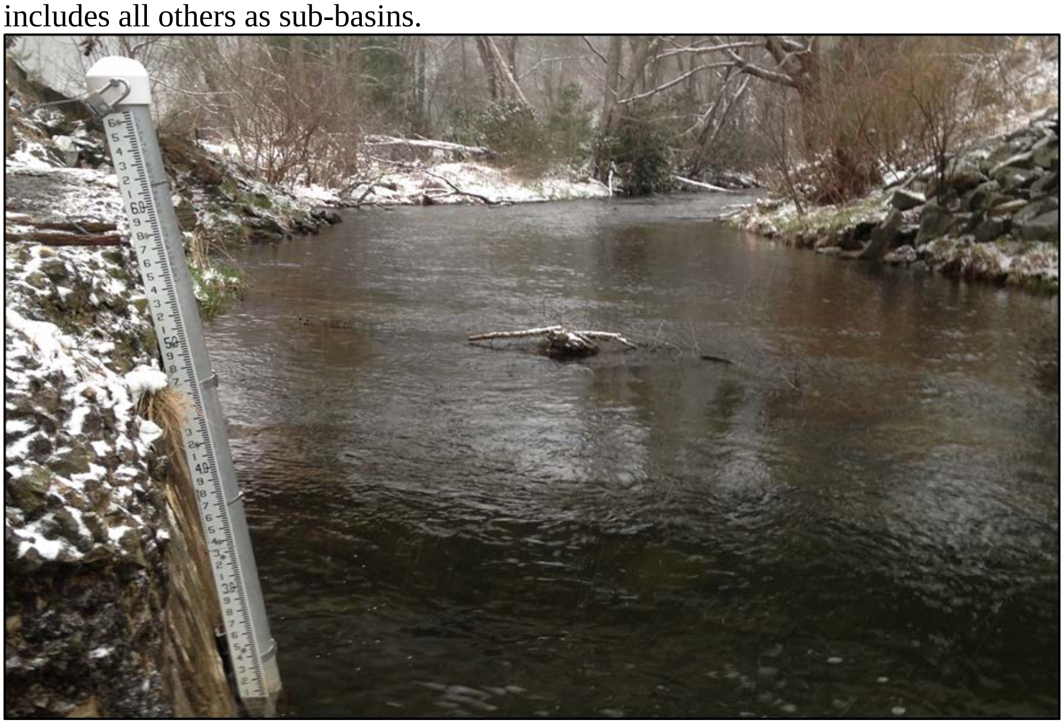

Figure 3.2. Installation for data logger with staff gauge; Middle Fork monitoring site.

Methods

Sample Collection

Water samples for Cl^- analysis were collected from each of the six AppAqua monitoring sites during precipitation events and at base flow conditions over the course of one year (August 2016 - August 2017). The intention of this method of sample collection is to capture Cl^- concentrations at a wide range of flow conditions representing the typical annual variability of discharges within the USF-NRW. Samples were collected using a depth integrated sampler (Figure 3.3) suspended into the stream above the thalweg (the deepest part of the channel). The body design of the sampler keeps the intake nozzle directed towards the flow of water. The sampler is raised and lowered from just above the streambed to just below the surface during collection in order to ensure accurate representation of stream constituent concentrations throughout the water column. Samples were immediately processed following collection, or were refrigerated for later processing, which occurred within 7 days of collection.

Figure 3.3. Depth integrated sampler; used for water sample collection

Sample Processing

Chloride concentration was determined for each sample using a Yellow Springs Instrument (YSI) Professional Plus Data Sonde that includes salinity, Cl^-, specific conductivity, and temperature sensors. The Cl^- sensor was calibrated prior to the analysis of each sample batch to maintain data integrity. Samples were poured into a 500 ml beaker, and the YSI Data Sonde was inserted into the sample and held in place until the Cl^- reading stabilized. Additionally, specific conductivity was recorded for each of the samples to verify the relationship between the two variables, as specific conductivity is often used as a proxy for Cl^- (Granato & Smith, 1999, Morgan et al. 2012, Perera, Gharabaghi & Howard, 2013).

Data Analysis

First, impervious surface area and road network density were determined for each of the sub-basins and correlated with the median Cl^- concentrations within each basin. The drainage network extraction and watershed delineation modules included in the ArcHydro extension of ArcGIS 10.4 (Maidment, 2002) were used to delineate sub-basins from LiDAR data (North Carolina Floodplain Mapping Program, 2016). This data is provided in 10,000 ft. by 10,000 ft. tiles and has a 20 ft. resolution. A high-resolution impervious surface layer was used to quantify impervious surface area within the sub-basins (Carlyle, 2013). Impervious surfaces were classified from NAIP imagery with a 2 meter resolution using the Feature analyst extension for ESRI ArcGIS. Impervious surfaces were then resampled to a 20 ft. resolution to match the resolution of the sub-basins. Road network density was determined within each of the sub-basins using Integrated Statewide Road Network data provided by the North Carolina Department of Transportation (North Carolina Department of Transportation, 2007). Road network density was simply determined as the ratio of the length of roads to the sub-basin drainage area. The relationships were then modeled using ordinary least squares (OLS) regression.

Next, differences between sub-basins, and seasonal variations were investigated. The basic descriptive statistical characteristics (range, median, etc.) of chloride were determined for each sub-basin, and for each season for initial comparison. Then, all chloride data was stratified by season and compared using a Tukey Multiple Comparison test in order to identify possible differences in seasonal mean Cl^- concentrations throughout the basin as a whole.

Next, relationships between discharge (Q) and Cl^- concentration were investigated using OLS regression and an analysis of hysteresis. Discharge (CFS) at the time of sample collection was determined by converting the stage measurement (as recorded by the AppAqua data loggers) to discharge using a stage/discharge rating curve that had previously been developed for each site. Ordinary least squares regression was used to model the discharge/concentration relationships and evaluated based on typical OLS diagnostics. The existence of hysteresis was investigated by plotting the Q/ Cl^- data relative to its position on the stream hydrograph, i.e., rising limb versus falling limb, and assessing the characteristics of the hysteretic loops, if they occurred.

Finally, Cl^- toxicity trends were evaluated based on the six-year conductivity record recorded by the AppAqua monitoring stations. The relationship between Cl^- and conductivity in the field samples were modeled using a simple linear regression. The linear model was then used to determine Cl^- concentrations for the six year record. The Cl^- time series was then evaluated relative to the thresholds of acute and chronic Cl^- toxicity as determined by the U.S. Environmental Protection Agency.

Results and Discussion

Timing of Sample Collection

Over the course of the year-long sampling campaign 27 samples were collected over a wide range of hydrologic conditions and during each of the four seasons. Five samples were collected during the fall, 11 during the winter, 6 during the spring, and 4 during the summer. Approximately 22% of samples were collected during baseflow conditions, while 48% were collected during the rising limb of the hydrograph and 30% were collected during the falling limb of the hydrograph. Figure 4.1 shows the sample collection dates relative to the stage hydrograph for each sub-basin provided by the in-situ data loggers. Unfortunately, intermittent equipment malfunction resulted in gaps in the stage data for several of the sub-basins, many of which coincided with sample collection dates. In some instances, manually recorded staff gauge measurements were available to provide stage data for theses gaps. Additionally, stage was recorded by the sondes at some locations in instances where the water level dropped below the location of the instrument. For select sub-basins, this resulted in gaps in the stage record that limited the extent of our analysis. Specifically, the incomplete stage for Hodges Creek, Winkler's Creek, Middle Fork and the State Farm sub-basins was insufficient to establish accurate discharge/Cl^- rating curves. The relatively complete stage records, and previously established stage/discharge rating curves for Boone Creek and Goshen Creek allowed us to investigate concentration/discharge trends, and make comparisons between the most developed and least developed sub-basin. Although stage data was incomplete for the other sub-basins, it was still possible to make general comparisons of Cl^- concentrations between basins, and between seasons.

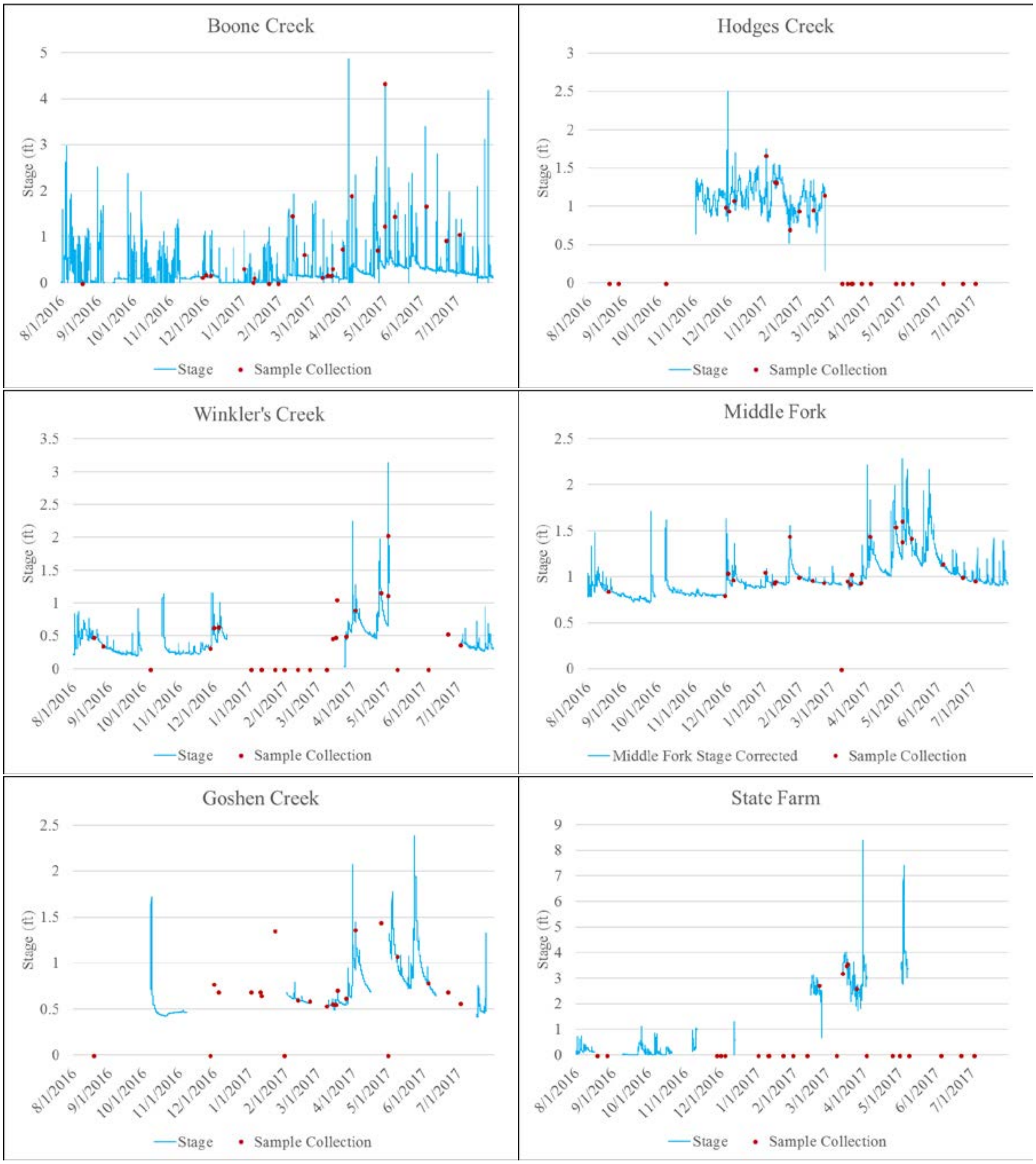

Figure 4.1: Sub-basin stage record and sample collection points in relation to hydrograph

Impacts of Roads and Impervious Surfaces

Since Cl^- concentrations in streams are known to be affected by road salt application, the analysis of Cl^- in USF-NRW streams began with an analysis of road network density and impervious surface percentages in the study basins (Figure 4.2). Considerable differences in impervious surface and road network density exist across our 6 sub-basin sites (Table 4.1). As expected, Boone Creek and Hodges Creek exhibit the highest concentration of roads (0.82 and 0.71 respectively) and the greatest amount of impervious surfaces (28.1% and 17.8% respectively). Winkler's Creek and Goshen Creek have considerably less. Our largest sub-basin, the Middle Fork, and the entire USF-NRW watershed (State Farm), have impervious surface and road network densities that are relatively intermediate.

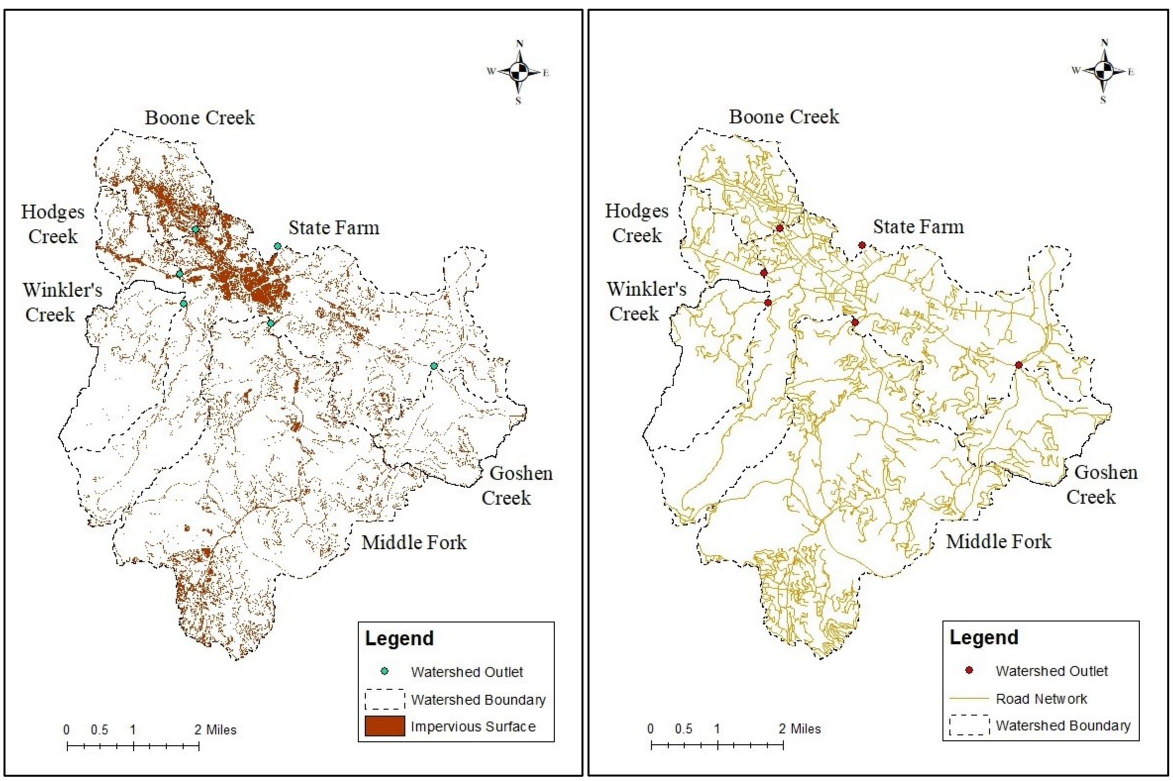

Figure 4.2. Impervious surface (Carlyle, 2013) and road network density (NCDOT, 2007) in the USF-NRW

Table 4.1 Basin area, road network density and impervious surface by sub-basin

Sub-basin	Boone Creek	Hodges Creek	Winkler's Creek	Middle Fork	Goshen Creek	(USF-NRW) State Farm
Road Network Density	0.82	0.71	0.28	0.61	0.60	0.55
Impervious Surface (%)	28.10	17.37	4.50	12.22	7.54	13.87

Median Cl^- concentrations from each sub-basin were regressed on both road network density and impervious surface (Figure 4.3). Both road network density and impervious surface exhibit a power-law relationship with median Cl^- concentration whereby increases in road network density and impervious surface result in increases in median Cl^-. The relationship is strong for impervious surface and median Cl^- values ($R^2 = 0.9307$) and somewhat weaker for road network density ($R^2 = 0.5513$). This potentially suggests that the magnitude of runoff, which is higher for impervious surface, is as important a factor, if not more important, than the density of the road network. A potential explanation for this could be that the resolution of road network data, which calculates length but not width of roads, limits the strength of the power-law relationship. This could also suggest that the proximity of roads from streams is important, or that salt application on sidewalks and parking lots is also an important contributor to Cl^- concentration.

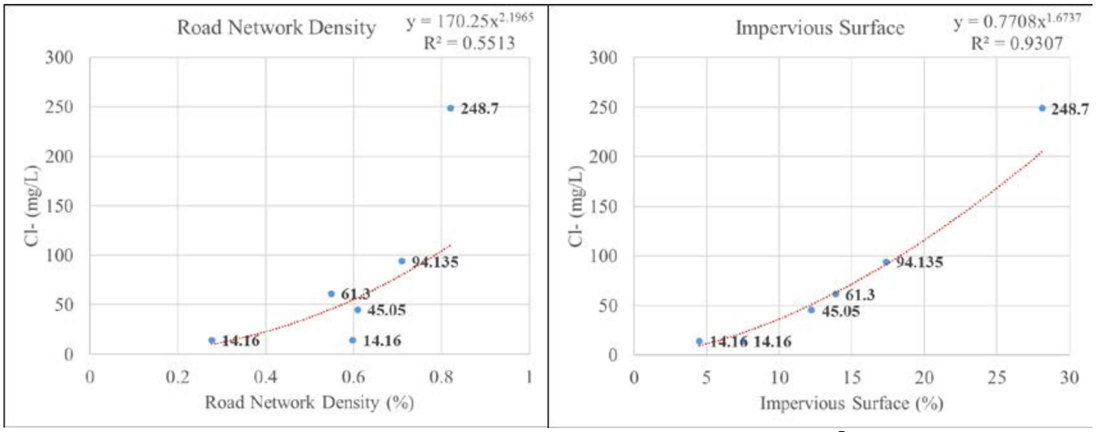

Figure 4.3 Relationship between Cl^- and road network density ($R^2 = 0.5513$) and impervious surface ($R^2 = 0.9307$)

Comparison between Basins and Seasons

Median Cl^- concentrations ranged from 14.16 mg/L at the Winkler's Creek and Goshen Creek stations to 248.7 mg/L at the Boone Creek station. Boone Creek displayed the widest range of Cl^- concentrations (1337.81 mg/L) and the highest recorded concentration (1348.86 mg/L) among the sub-basins. This is not surprising as Boone Creek is the most developed sub-basin as compared to Winkler's Creek, the least developed sub-basin. A boxplot comparison between basins is provided in Figure 4.4

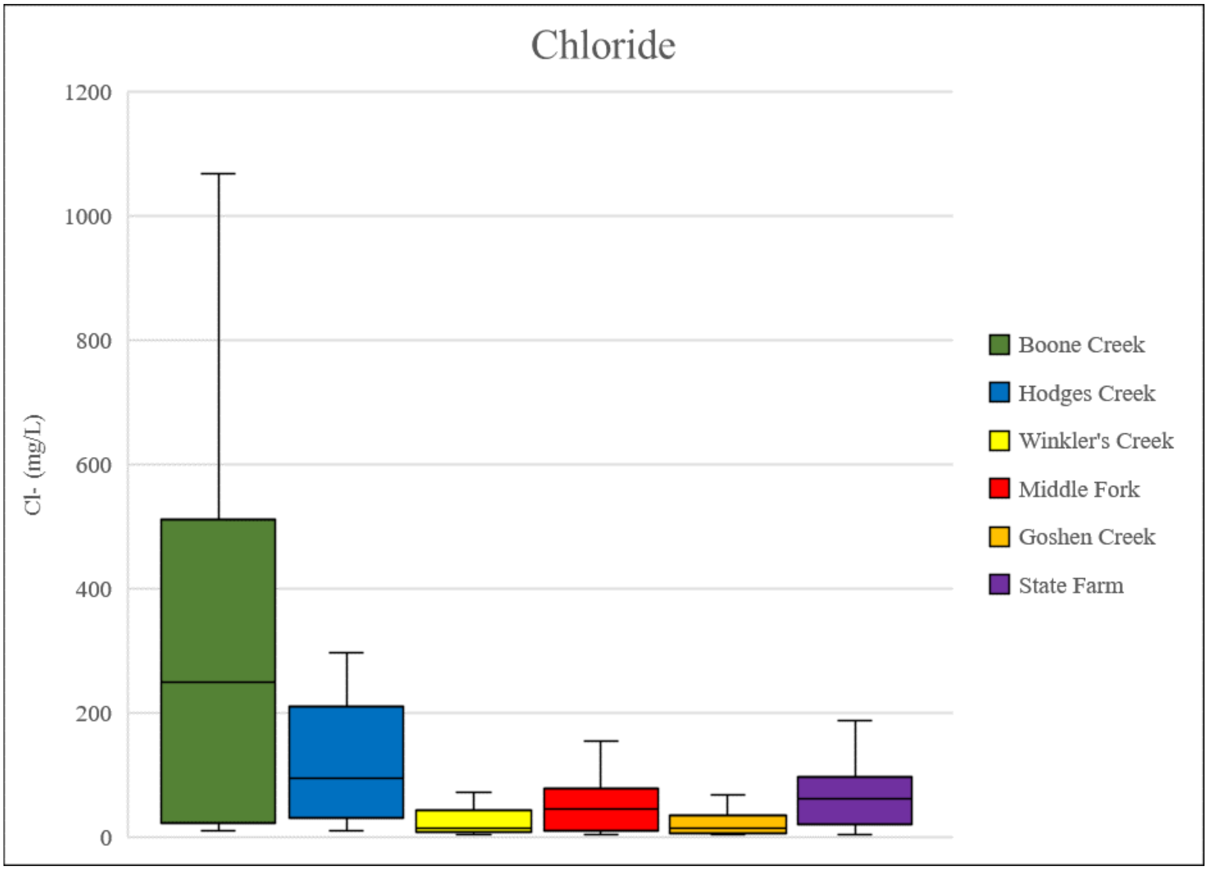

Figure 4.4 Annual Cl^- characteristics by sub-basin

The differences in sub-basin Cl^- concentrations are equally apparent in seasonal trends. Figure 4.5 shows maximum seasonal Cl^- concentrations for each watershed over the course of the one-year study period. High seasonal values in Cl^- concentration correspond with the winter months and occur most notably in the highly developed sub-basins. From spring to winter, a trend of increasing maximum Cl^- concentration is observed in all of the basins with the exceptions of Winkler’s Creek and Goshen Creek, which are the watersheds with the least amount of urban development (4.5% and 7.5 % impervious surface respectively). Relatively high Cl^- values for all of the sub-basins in autumn are likely a result of seasonally low base-flow conditions and an increased concentration of Cl^- that has been stored in soils or groundwater.

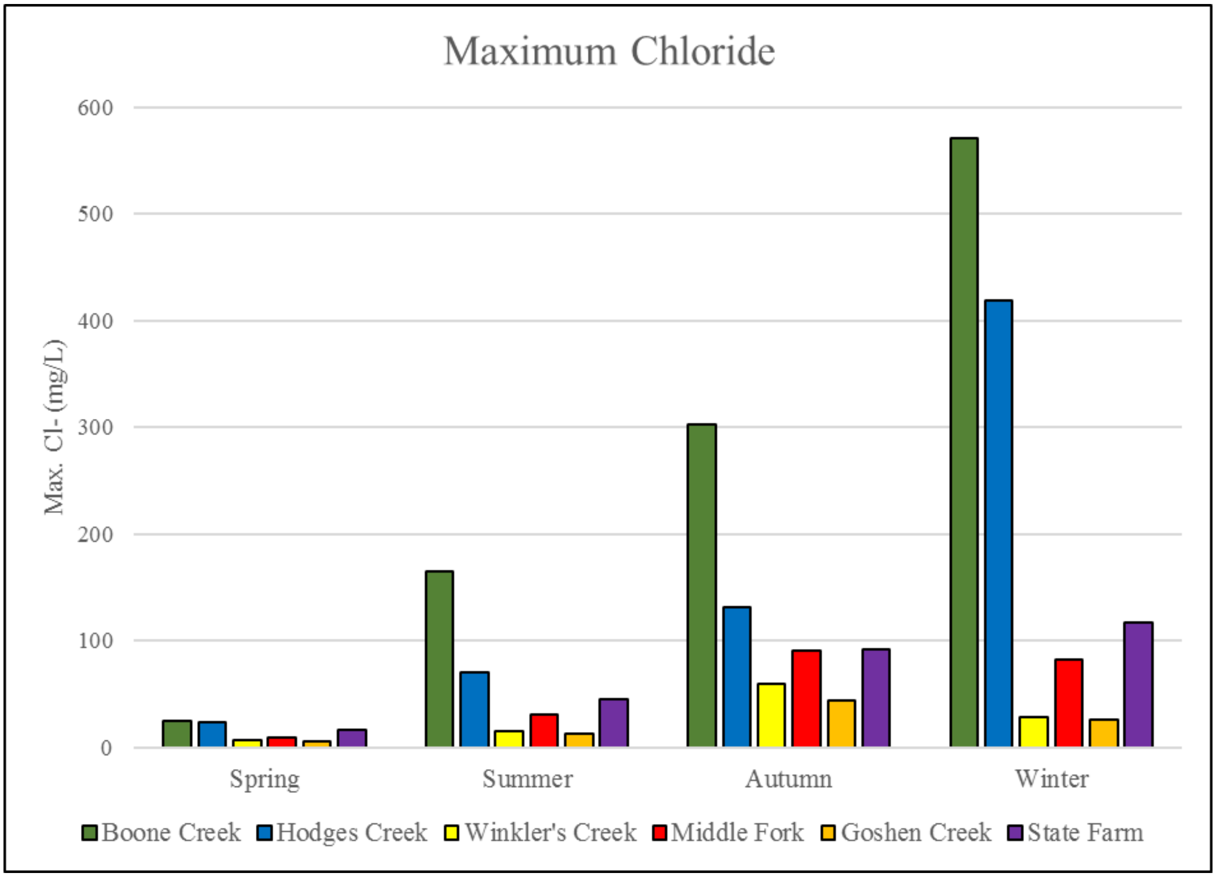

Figure 4.5 Seasonal maximum Cl^- characteristics by sub-basin

Seasonal differences in maximum Cl^- concentration were confirmed using a Tukey Multiple Comparison AOV test (Figure 4.6). Winter Cl^- values were significantly higher than both spring and summer Cl^- values (a = 0.05). These results are in agreement with our expectation, and with other studies (Gardner & Royer, 2010, Kelly et al. 2008), that show Cl^- concentrations are elevated during winter months, when road salt is applied.

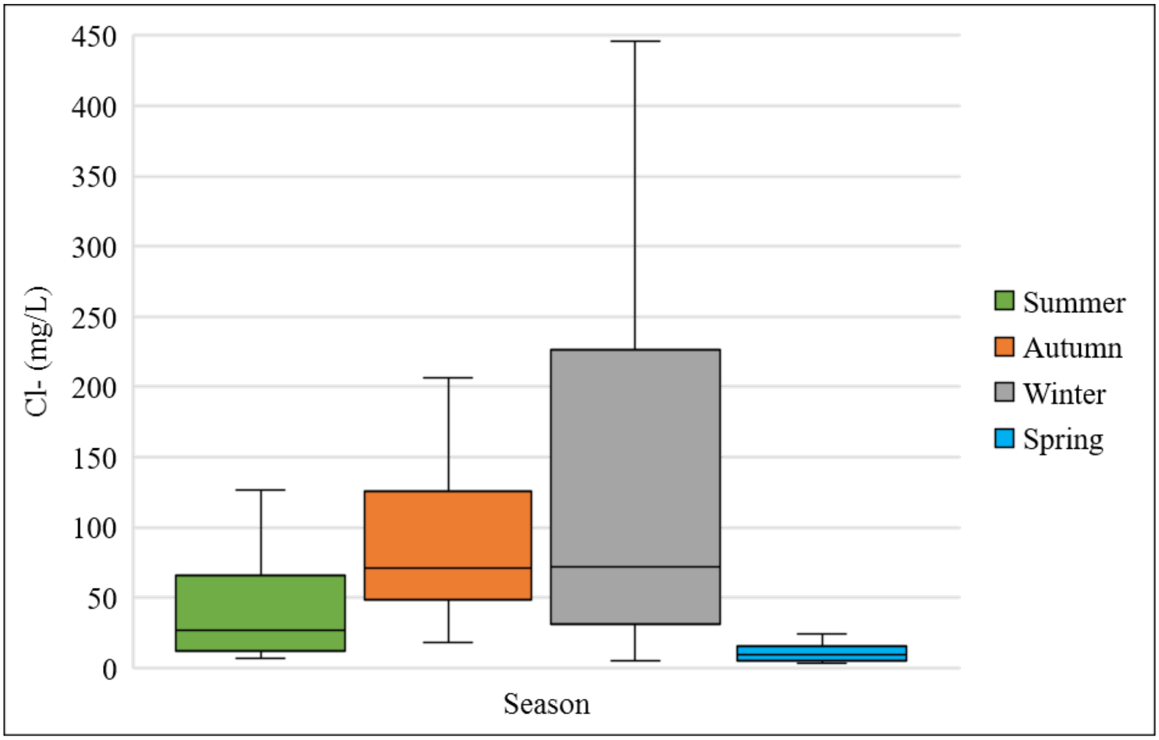

Figure 4.6 Boxplot comparing maximum Cl^- concentrations between seasons

Cl^-/Discharge Relationship

Discharge values were calculated for Boone Creek and Goshen Creek during sample collection times using stage/discharge rating curves that had previously been developed for AppAqua research investigations (Figure 4.7).

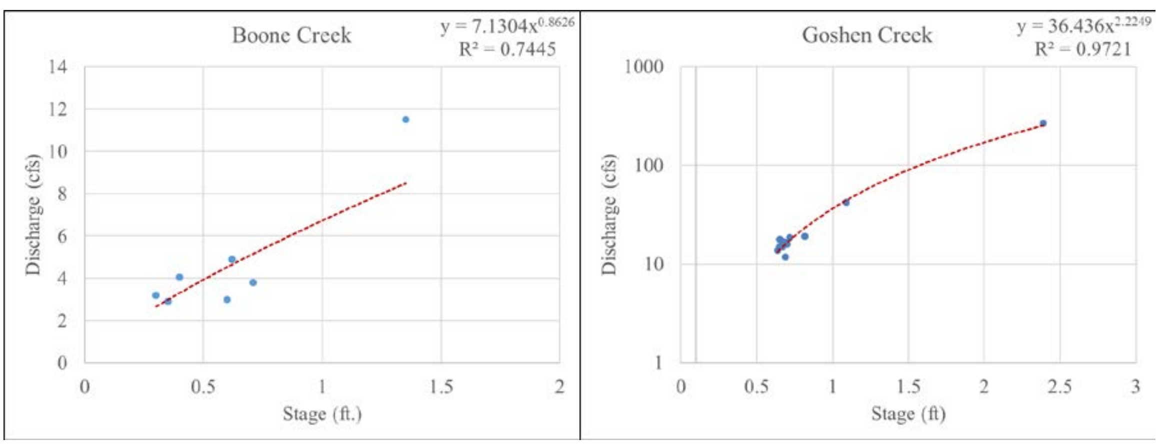

Figure 4.7 Stage discharge curves for Boone Creek ($R^2 = 0.7445$) and Goshen Creek ($R^2 = 0.9721$)

The stage records for both Boone Creek and Goshen Creek were relatively complete which made it possible to determine the discharge associated with the majority of the water quality samples, and made it possible to investigate the relationship between discharge and Cl^- concentration for both sub-basins (Figure 4.8). These relationships were also best modeled as power-law functions, however, neither basin exhibited a particularly strong relationship between Cl^- and discharge (Boone Creek $R^2 = 0.58$, Goshen Creek $R^2 = 0.02$). Both sites, however, showed a similar pattern of increasing Cl^- concentrations to a point, followed by decreasing concentrations as discharge continues to increase.

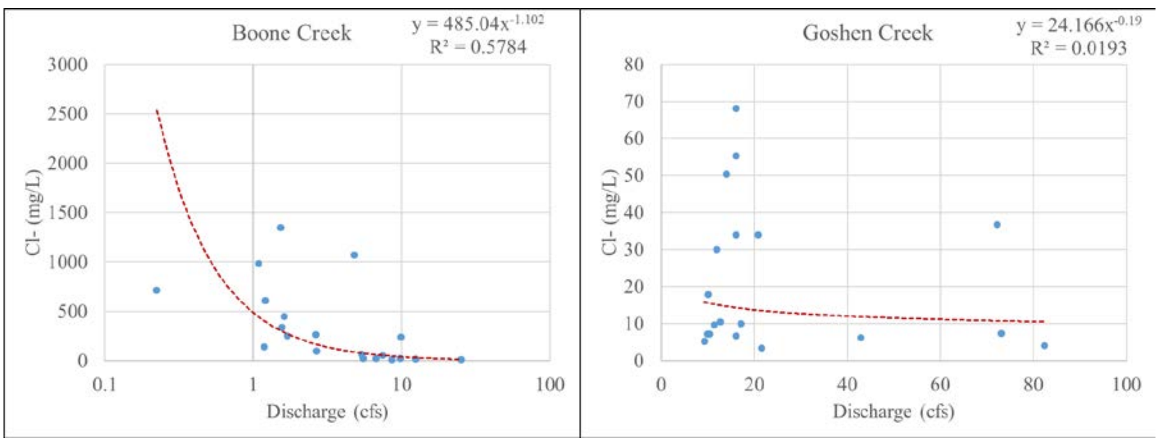

Figure 4.8 Discharge/Cl^- relationship at Boone Creek ($R^2 = 0.5786$) and Goshen Creek ($R^2 = 0.0193$)

Although most of the sample collections occurred at, or close to peak flow conditions, the higher Cl^- concentrations correspond primarily with lower discharge values for both sub-basins. These results suggest that both hysteresis, as well as seasonal trends in Cl^- concentration, may complicate the relationship between discharge and Cl^-, and suggest that OLS regression is not sufficient for modeling this relationship

To further investigate the influence of hysteresis on Cl^-/discharge relationships, Cl^- values were determined from the entire period of record based on its relationship with conductivity. It is well known that there is a strong relationship between specific conductivity and Cl^-, in fact research has shown that specific conductivity is such a reliable proxy that it can be used in lieu of Cl^- measurements for some purposes (Granato & Smith, 1999, Morgan et al. 2012, Perera et al. 2013). In accordance with these studies, specific conductivity and Cl^- also exhibit a strong linear association in the USF-NRW (R^2 = 0.85) (Figure 4.11). This linear model was deemed an acceptable means of back-calculating Cl^- concentrations from conductivity measurements in the USF-NRW.

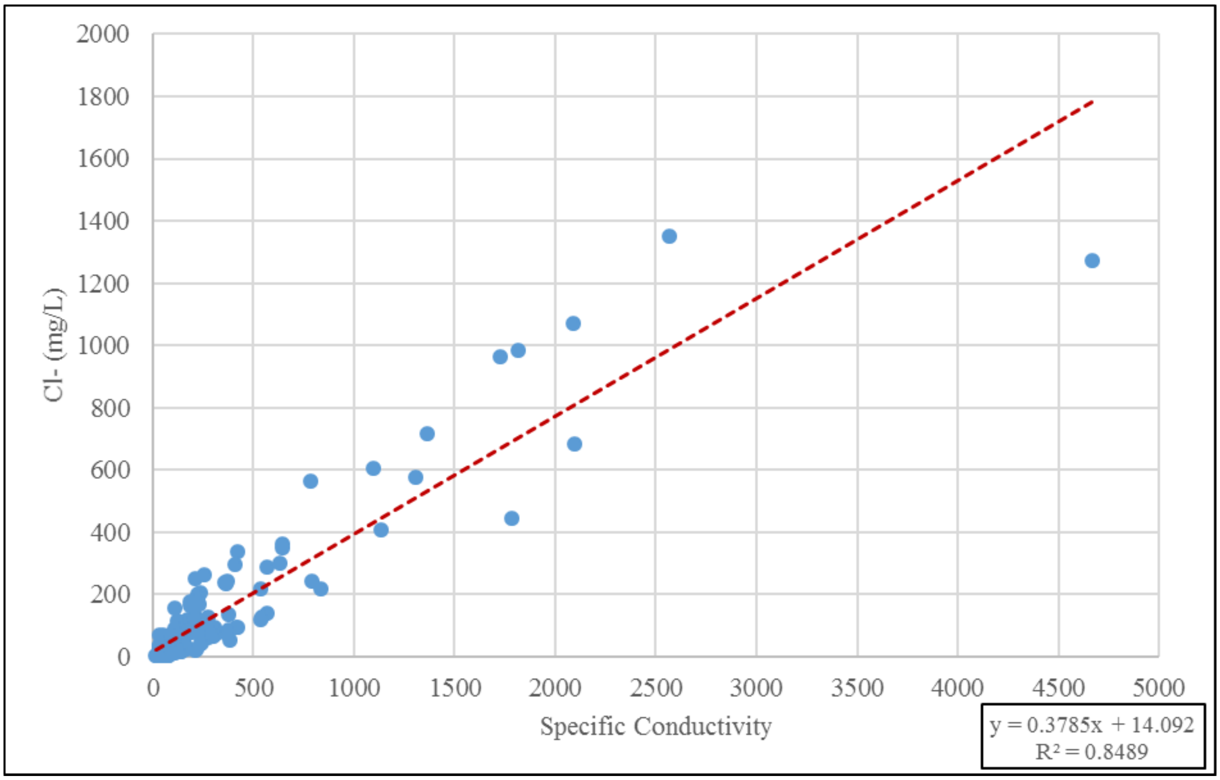

Figure 4.9 Relationship between specific conductivity and Cl^- (R^2 = 0.8489) established from water quality samples

The conductivity record allowed us to further investigate the possible influence of hysteresis on the relationships between Cl^- and discharge at both Boone Creek and Goshen Creek. Figure 4.9 shows all of the Cl^- values determined from the specific conductivity record that have a corresponding discharge measurement during the collection study period (August 2016-August 2017). It is again evident that an OLS power-law regression, although the best fitting, does not sufficiently model the relationship between Cl^- and discharge. However, it is again evident that high Cl^- values increase with discharge up to a point, and then decrease during the highest discharge values observed.

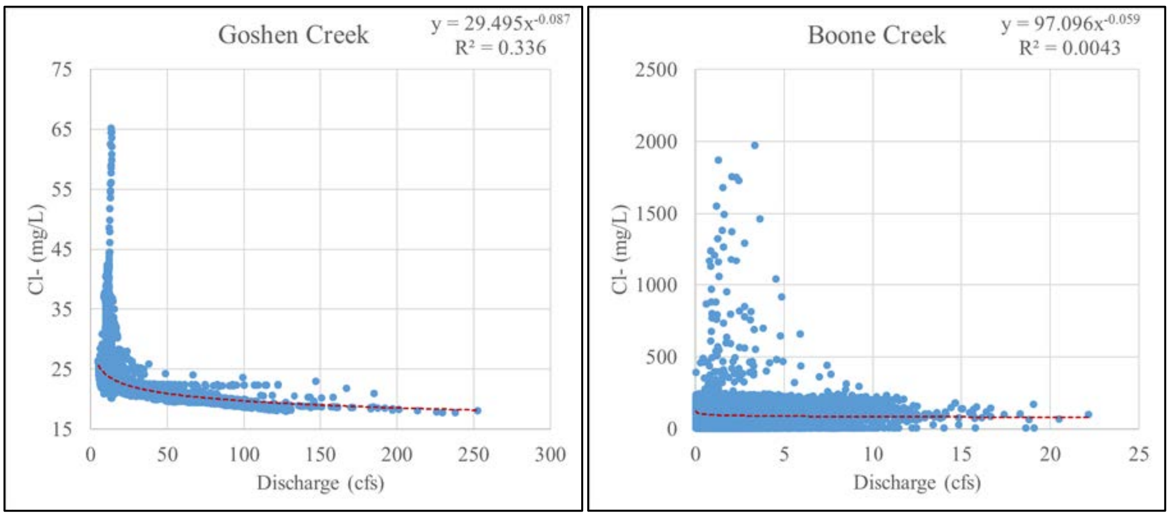

Figure 4.10 Cl^- and discharge for Boone Creek and Goshen Creek (Aug. 2016- Aug. 2017)

The possible influence of hysteresis in Goshen Creek and Boone Creek was investigated further by isolating notable elevated flow events throughout the study period and plotting the Cl^- values with respect to their position on the hydrograph (i.e. rising limb, falling limb). These events, plotted in Figure 4.10, are representative of all 4 seasons and the majority of them were analyzed for both sub-basins.

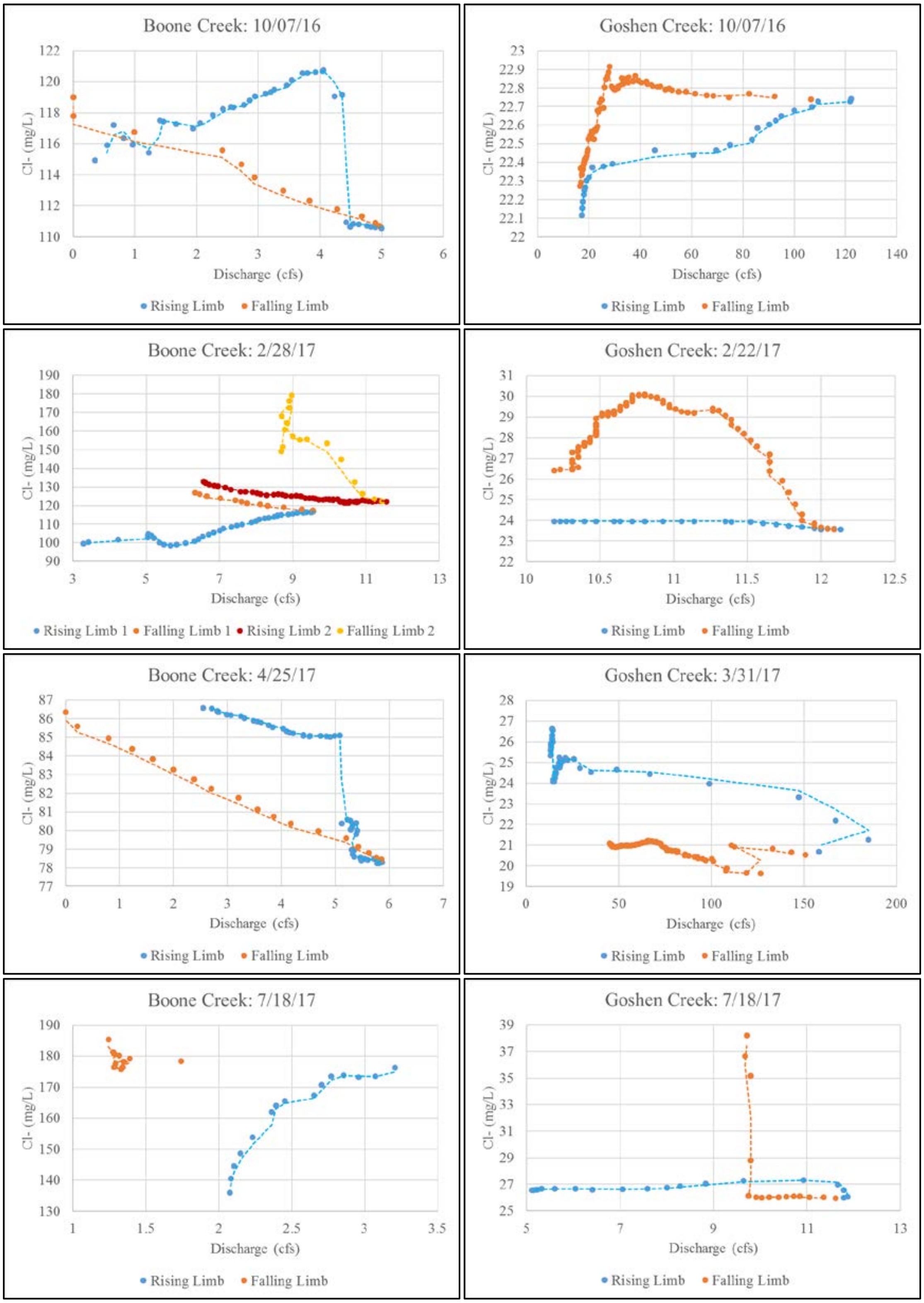

Figure 4.11 Chloride hysteresis in Boone Creek and Goshen Creek.

The apparent hysteretic character of Cl^- in Boone Creek is consistent with the expectation for an urbanized stream in several respects. The flashy nature of an urbanized stream is likely to result in an early flush of pollutant concentrations followed by a dilution during peak flows. Three of the events at Boone Creek (10/07/16, 2/28/17, 4/25/17) show a decrease in Cl^- while discharge values continue to rise, results that align with expectation. The dilution is remarkably abrupt for both the October and April event, which is expected from a hydrologic event in an urban stream. The rising limbs for all of the events at Boone Creek end with high Cl^- values, consistent with the expectation that ground water in Boone Creek has a relatively high Cl^- concentration.

In contrast to Boone Creek, the hysteresis in Goshen Creek shows a much more tempered response. For the latter three events (2/22/17, 3/31/17, 7/18/17) Cl^- values remain level or decrease moderately during the rising limb of an event. This corresponds well with the expectation that a forested watershed does not experience considerable surface runoff, and thus hydrologic response to precipitation is less dramatic and demonstrates more of a lag. Chloride values continue to rise during the falling limb for the majority of the Goshen creek events, and for the most part taper off toward a low base-flow concentration of Cl^-, which is consistent with the expectation for a forested watershed. In summary, based on the analysis of Boone Creek and Goshen Creek, the relationship between Cl^- and discharge is in fact hysteretic and therefore cannot be adequately characterized by ordinary least squares regression.

Cl^- Toxicity in the Upper South Fork of the New River

Using the Cl^-/Conductivity relationship discussed in the last section, Cl^- concentrations were determined for the entire period of record at all of the monitoring sites, using AppAqua's conductivity data. This provides a dataset extending from the summer of 2010 until the end of the study period in August of 2017 for all of the sub-basins with the exception of Hodges Creek. Figure 4.12 shows this Cl^- time series for each of the sub-basins. Each plot also displays the EPA chronic toxicity threshold of 230 mg/L and the acute toxicity threshold of 860 mg/L. The most notable peaks in Cl^- concentration occurred in the Boone Creek sub-basin, which over the 6-year record exceeded the acute threshold 1.14% of the time and the chronic threshold 8.23% of the time. These results agree with the study by Cockerill et al. (2017), which reported a chronic toxicity exceedance of 2% and an acute toxicity exceedance of 10% during one year. The average annual exceedance rates for Boone Creek were 6.7% for chronic toxicity and 0.6% for acute toxicity. In contrast, the Cl^- values in Winkler's Creek sub-basin do not exceed toxic levels during the entire record. Values for the entire USF-NRW (State Farm station) are intermediate with an exceedance rate of 0.04% of the time for acute toxicity and 1.03 % of the time for chronic toxicity over the six-year time series. The USF-NRW annual averages were 0.01% for acute toxicity and 0.7% for chronic toxicity.

Table 4.2 Toxicity exceedances for each sub-basin.

Sub-basin	Boone Creek	Winkler's Creek	Middle Fork	Goshen Creek	USF-NRW (State Farm)
Chronic Toxicity	8.23% 6.6% yr. Avg.	0.00%	0.07% 0.05% yr. Avg.	0.10% 0.08% yr. Avg.	1.03% 0.7% yr. Avg.
Acute Toxicity	1.14% 0.6 yr. Avg.	0.00%	0.00%	0.02% 0.02% yr. Avg.	0.04% 0.01% yr. Avg.

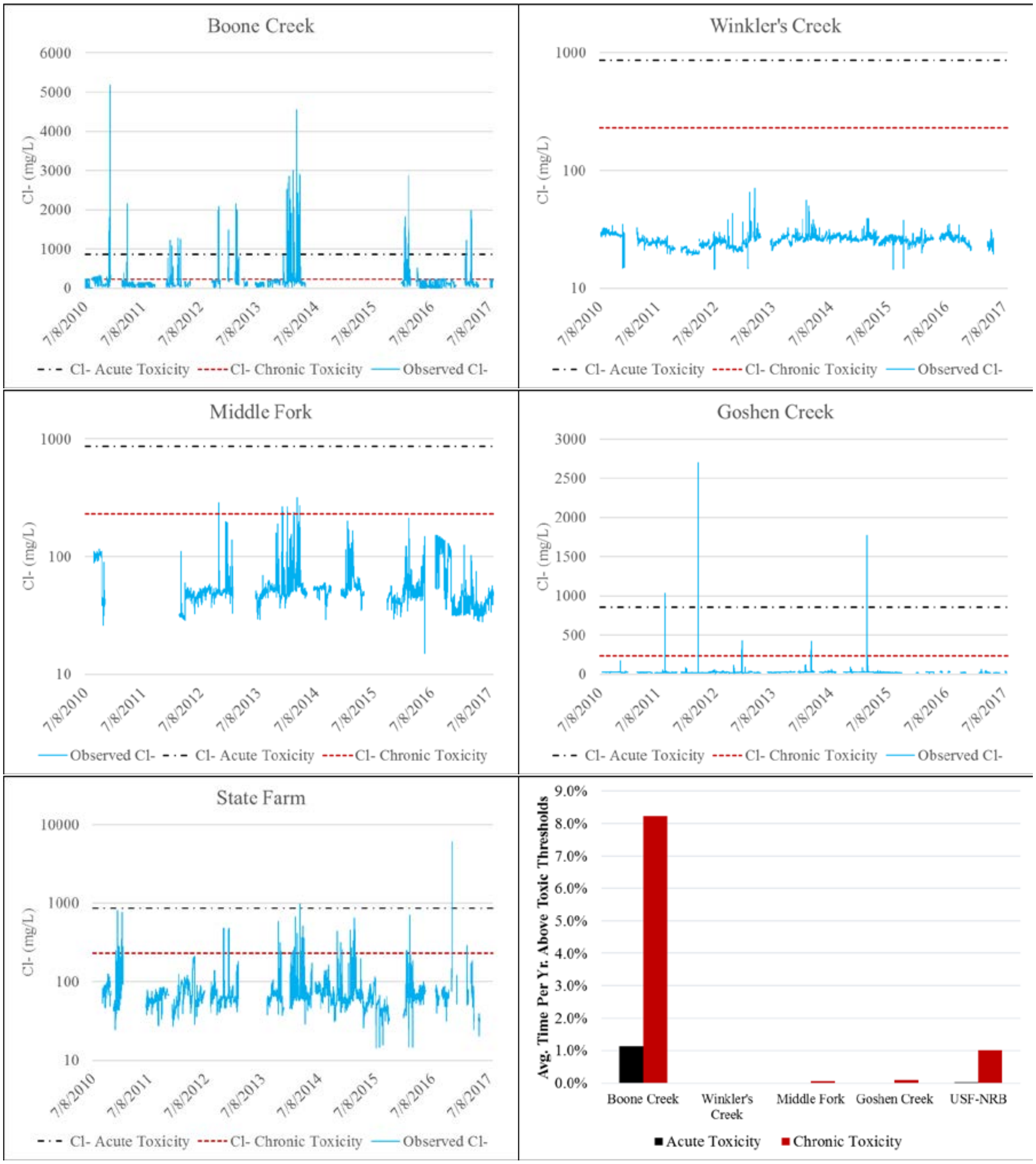

Figure 4.12 6-yr Cl^- trends for 5 sub-basins established by extrapolating Cl^- from specific conductivity; trends are plotted with EPA Cl^- toxicity thresholds (Acute 860 mg/L and Chronic 230 mg/L)

Conclusion

Anthropogenic activity has greatly contributed to the levels of Cl^- occurring in water resources throughout many regions of the United States as well as in the USF-NRW. The use of de-icing agents is critical for public safety, yet the application of road salts is not without impact on water resources. Although limited by an incomplete stage record, this research shows levels of Cl^- at or exceeding the EPA acute threshold 1.1% of the time and the chronic threshold 8.2% of the time in the most developed sub-basin. The entire watershed exceeds these thresholds 0.04% of the time (acute) and 1.03 % of the time (chronic). As expected, there is a clear seasonal influence on Cl^- concentrations, with the exception of the less developed sub-basins. This is in agreement with the expectation that winter months will have higher levels of Cl^- resulting from deicing salt application. A strong relationship exists between both impervious surface percentage and road network density and Cl^- concentration in USF-NRW sub-basins. This suggests that urbanization plays an influential role in the hydrologic controls responsible for transporting Cl^- into our streams. Finally, as demonstrated by Boone Creek and Goshen Creek, Cl^- response to precipitation events is hysteretic and thus not adequately characterized by simple OLS regression methods. Continued research on these controls and on Cl^- toxicity will be critical for on-going and future discourse pertaining to the management of de-icing salts in the USF-NRW, and in maintaining this ecologically important watershed.

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Appendix

Boone Creek Data

Date	Time of Collection	Chloride mg/L	Conductivity
8/19/2016	10:27 AM	286	570
8/27/2016	4:10 PM	301.5	633
9/26/2016	N/A	18	64.5
11/28/2016	1:21 PM	605.7	1095
12/1/2016	9:11 AM	248.7	212.1
12/5/2016	12:44 PM	338.2	420.8
1/2/2017	10:55 AM	262.49	256.4
1/10/2017	12:31 PM	715.01	1364
1/11/2017	3:02 PM	982.22	1818
1/23/2017	8:56 AM	576	1306
1/23/2017	8:58 AM	244.08	368
1/31/2017	9:55 AM	405.61	1137
2/12/2017	4:22 PM	241.61	793
2/22/2017	9:40 AM	1068.63	2087
3/9/2017	5:16 PM	140.52	568.6
3/14/2017	10:00 AM	446.25	1787
3/17/2017	7:07 PM	1348.86	2569
3/18/2017	7:12 AM	95.52	415.3
3/26/2017	10:44 AM	23.77	169.4
4/3/2017	1:55 PM	15.36	73.6
4/25/2017	10:11 AM	66.15	298
5/1/2017	9:17 AM	12.57	95.7
5/1/2017	12:48 PM	11.05	61.3
5/9/2017	8:53 AM	21.41	125.2
6/5/2017	4:42 PM	N/A	N/A
6/22/2017	1:17 PM	21.1	212
7/3/2017	1:33 PM	51.4	385.3

Hodges Creek

Date	Time of Collection	Chloride mg/L	Conductivity
8/19/2016	11:03 AM	87	247
8/27/2016	4:29 PM	126.4	277
10/7/2016	N/A	79.4	130.1
11/28/2016	1:32 PM	126	210
12/1/2016	9:22 AM	113.2	219.5
12/5/2016	12:54 PM	206.4	238.7
1/2/2017	11:09 AM	189.57	225.7
1/10/2017	12:40 PM	561.8	782
1/11/2017	3:12 PM	961.85	1728
1/23/2017	9:10 AM	167.34	231.7
1/31/2017	10:23 AM	218.97	538.7
2/12/2017	4:32 PM	94.55	309.1
2/22/2017	10:02 AM	296.27	409.6
3/9/2017	5:31 PM	72.18	287.4
3/14/2017	10:12 AM	1271.92	4665
3/17/2017	7:17 PM	683.44	2095
3/18/2017	7:22 AM	93.72	425
3/26/2017	10:58 AM	59.51	277
4/3/2017	2:06 PM	22.73	104.5
4/25/2017	10:19 PM	33.51	120.8
5/1/2017	9:26 AM	9.84	107.3
5/1/2017	12:58 PM	10.58	59.7
5/9/2017	8:59 AM	15.9	60.2
6/5/2017	4:59 PM	14.52	140.5
6/22/2017	1:25 PM	25.22	218.93
7/3/2017	1:45 PM	44.38	242.8

Winkler's Creek

Date	Time of Collection	Chloride mg/L	Conductivity
8/19/2016	11:22 AM	N/A	N/A
8/27/2016	6:50 PM	27.5	43.5
10/7/2016	N/A	56.4	43.4
11/28/2016	1:42 PM	71.3	55.9
12/1/2016	9:30 AM	47.3	45
12/5/2016	1:03 PM	63.6	44.4
1/2/2017	11:15 AM	54.92	49.6
1/10/2017	12:48 PM	40.67	37.9
1/11/2017	3:18 PM	32.8	40.8
1/23/2017	9:16 AM	66.5	60.8
1/31/2017	10:31 AM	40.62	42.1
2/12/2017	4:38 PM	23.75	33.1
2/22/2017	10:09 AM	14.72	54
3/9/2017	5:37 PM	9.18	42.1
3/14/2017	10:24 AM	14.16	72.6
3/17/2017	7:25 PM	13.74	53.8
3/18/2017	7:33 AM	7.68	54.2
3/26/2017	11:05 AM	11.85	41.8
4/3/2017	2:12 PM	5.36	29
4/25/2017	10:27 AM	7.93	33.2
5/1/2017	9:33 AM	3.8	31.8
5/1/2017	1:06 PM	5.59	29
5/9/2017	9:05 AM	6.2	26.5
5/9/2017	9:06 AM	6.41	27.6
6/5/2017	5:07 PM	5.06	34.1
6/22/2017	1:32 PM	7.85	42.6
7/3/2017	1:50 PM	9.37	40.1

Middle Fork

Date	Time of Collection	Chloride mg/L	Conductivity
8/19/2016	1:02 PM	59	98.2
8/27/2016	N/A	42	109.2
10/7/2016	N/A	N/A	N/A
11/28/2016	1:53 PM	69.4	110
12/1/2016	9:46 AM	48.1	85.6
12/1/2016	9:44 AM	61.7	90.9
12/5/2016	1:13 PM	154.4	111.2
1/2/2017	11:25 AM	82.02	134.5
1/10/2017	1:00 PM	87.03	114.9
1/11/2017	3:28 PM	234.45	362.5
1/11/2017	3:30 PM	237.1	355.5
1/23/2017	9:24 AM	67	93
1/31/2017	10:40 AM	51.95	127.2
2/12/2017	4:47 PM	58.86	113.1
2/22/2017	10:18 AM	17.48	121.5
3/9/2017	5:46 PM	15.81	107
3/14/2017	10:44 AM	117.34	539.3
3/14/2017	10:45 AM	126.07	545.8
3/17/2017	7:33 PM	N/A	N/A
3/18/2017	7:43 AM	87.6	378.9
3/26/2017	11:16 AM	23.51	132.1
4/3/2017	2:23 PM	10.65	77.8
4/25/2017	10:35 PM	9.45	71.7
5/1/2017	9:43 AM	3.69	75.7
5/1/2017	1:16 PM	5.39	75.6
5/9/2017	9:14 AM	10.06	75.4
6/5/2017	5:16 PM	5.2	59
6/22/2017	1:53 PM	9.5	85.9
7/3/2017	2:09 PM	12.67	99.1

Goshen Creek

Date	Time of Collection	Chloride mg/L	Conductivity
8/19/2016	12:44 PM	18	41
8/27/2016	N/A	20.1	39.2
10/7/2016	N/A	41.4	40.5
11/28/2016	2:08 PM	34.7	43.1
12/1/2016	10:10 AM	34	33.4
12/5/2016	1:29 PM	68.1	35.4
1/2/2017	11:38 AM	55.28	54.1
1/10/2017	1:10 PM	33.96	34.2
1/11/2017	3:41 PM	50.37	68.9
1/23/2017	9:35 AM	36.81	34.5
1/31/2017	10:51 AM	28.36	56.3
2/12/2017	5:00 PM	30.02	41.1
2/22/2017	10:29 AM	9.58	45.6
3/9/2017	5:57 PM	5.21	38
3/14/2017	11:03 AM	17.92	84.3
3/17/2017	7:45 PM	7.23	40
3/18/2017	7:55 AM	10.02	82.6
3/26/2017	11:29 AM	10.4	42
4/3/2017	2:33 PM	7.37	36.1
4/25/2017	10:47 AM	3.96	30.7
5/1/2017	10:01 AM	3.26	32.6
5/1/2017	1:28 PM	4.96	32.3
5/9/2017	9:25 AM	6.21	32.5
6/5/2017	5:30 PM	3.32	18.1
6/22/2017	2:45 PM	6.6	35
7/3/2017	2:40 PM	7.13	35.8

State Farm

Date	Time of Collection	Chloride mg/L	Conductivity
8/19/2016	11:47 AM	N/A	N/A
8/27/2016	5:02 PM	90.2	160.4
10/7/2016	N/A	118	174.3
11/28/2016	2:41 PM	113.4	169
12/1/2016	10:47 AM	61.3	92.9
12/5/2016	1:53 PM	74.7	97.9
1/2/2017	12:08 PM	103.68	153.5
1/10/2017	1:49 PM	188.26	220
1/11/2017	4:14 PM	349.92	646.4
1/23/2017	10:05 AM	59.6	92
1/31/2017	11:22 AM	80.48	246
2/12/2017	5:38 PM	85.39	251.8
2/22/2017	11:07 AM	39.22	240.1
3/9/2017	6:35 PM	23.67	136.8
3/14/2017	11:25 AM	217.06	837
3/17/2017	8:04 PM	71.71	370.6
3/18/2017	8:12 AM	72.12	316.2
3/26/2017	11:51 AM	59.71	241.8
4/3/2017	2:50 PM	24.49	79.5
4/25/2017	11:23 PM	3.13	16.3
5/1/2017	10:26 AM	5.6	69.3
5/1/2017	1:44 PM	5.05	50.7
5/9/2017	9:45 AM	10.83	84.3
6/5/2017	5:46 PM	9.65	69.6
6/22/2017	3:08 PM	27.63	176.7
7/3/2017	2:59 PM	17.13	137.9

Vita

James Zebulon Sanders was born in Boone, North Carolina, to Jim and Lynn Sanders. He graduated from Watauga High School in the Spring of 2008 and enrolled at Appalachian State University the following Autumn. He graduated from Appalachian State University with a Bachelor of Arts in Geography in May 2012. In the fall of 2016, he accepted a research assistantship in Geography at Appalachian State University and began study toward a Master of Arts degree, which he received in May 2018. After graduating, he intends to pursue a Ph.D. in geography and ultimately a career in education or resource conservation.